Copolyimides Containing Surface Modifying Groups: Competition Between Silicone and Fluorine-Containing Blocks

Christopher J. Wohl[1], Allison M. Crow[2], William T. Kim[2], Michelle H. Shanahan[3], Jereme R. Doss[3], Yi Lin[3], John W. Connell[1]

[1]NASA Langley Research Center, Hampton, VA 23681
[2]Langley Aerospace Research Summer Scholar (LARSS), NASA Langley Research Center, Hampton, VA, 23681
[3]National Institute of Aerospace, Hampton, VA 23666

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Surface Modifying Agents (SMA)s in Action

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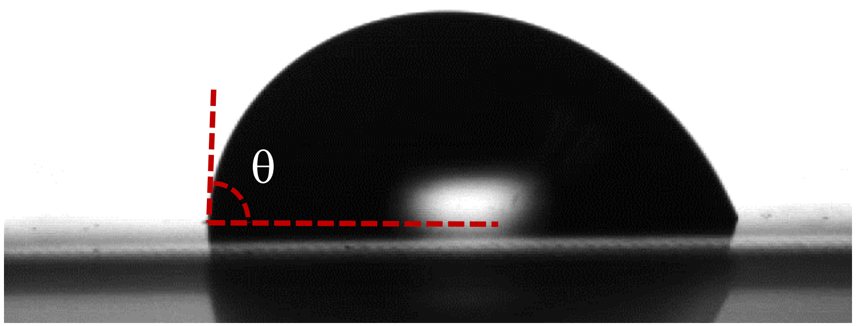
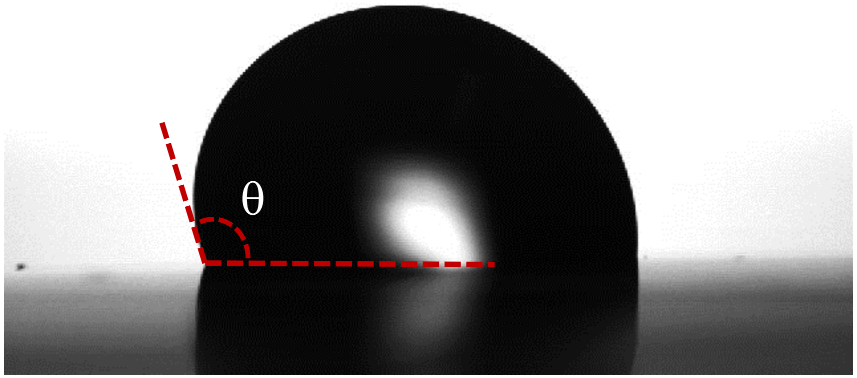
Polyimide without SMAs

89°



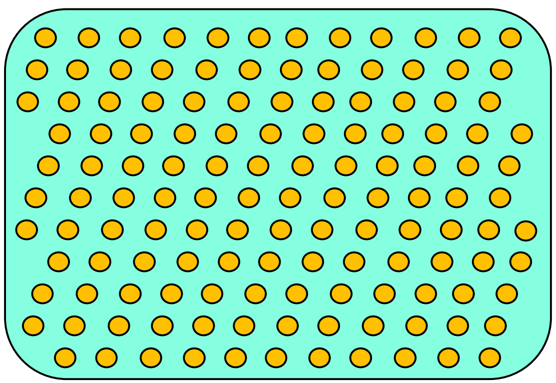
Polyimide with SMAs

116°

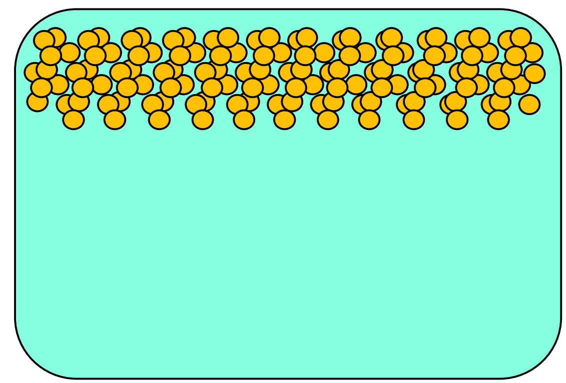


8 μL water droplet tilting axis contact angle experiment

- **Entropy vs enthalpy**



Entropically Favorable Distribution

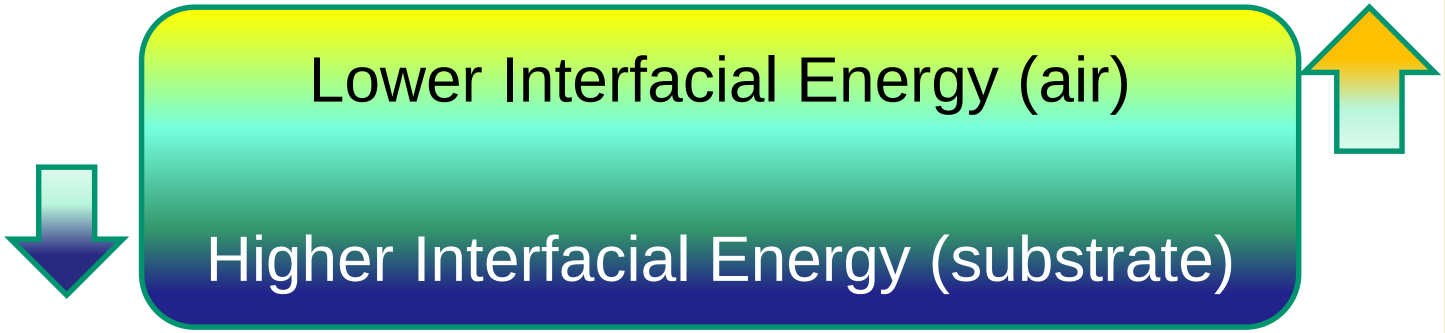


Enthalpically Favorable Distribution

Surface Migration

- **Entropy vs enthalpy**

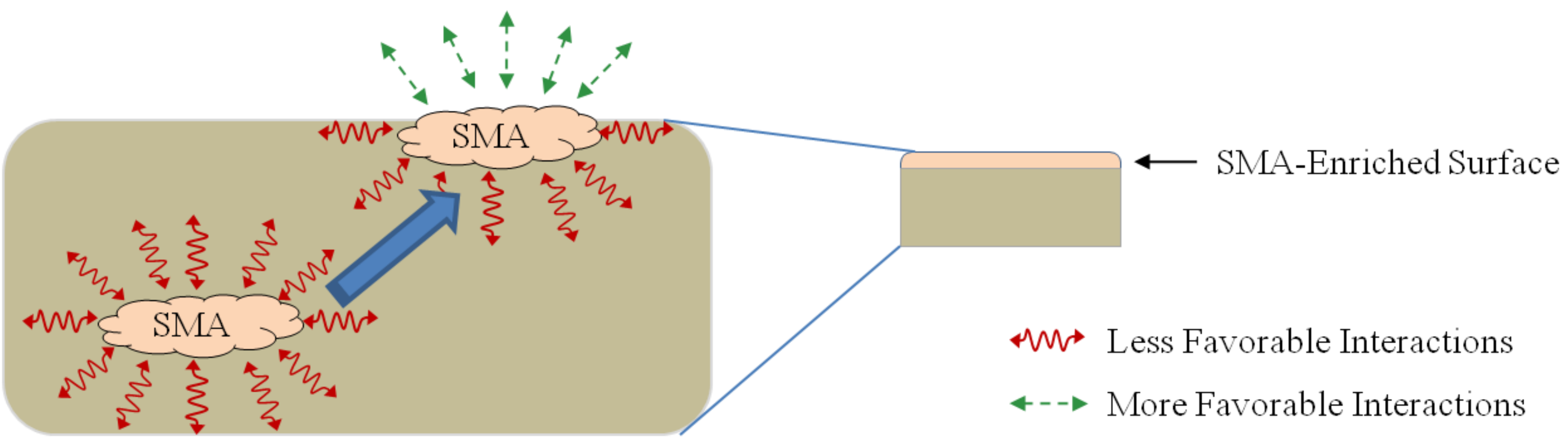
Thermodynamic Response of SMA



Arrows indicate enthalpy-driven migration of **LOW** and **HIGH** surface energy components

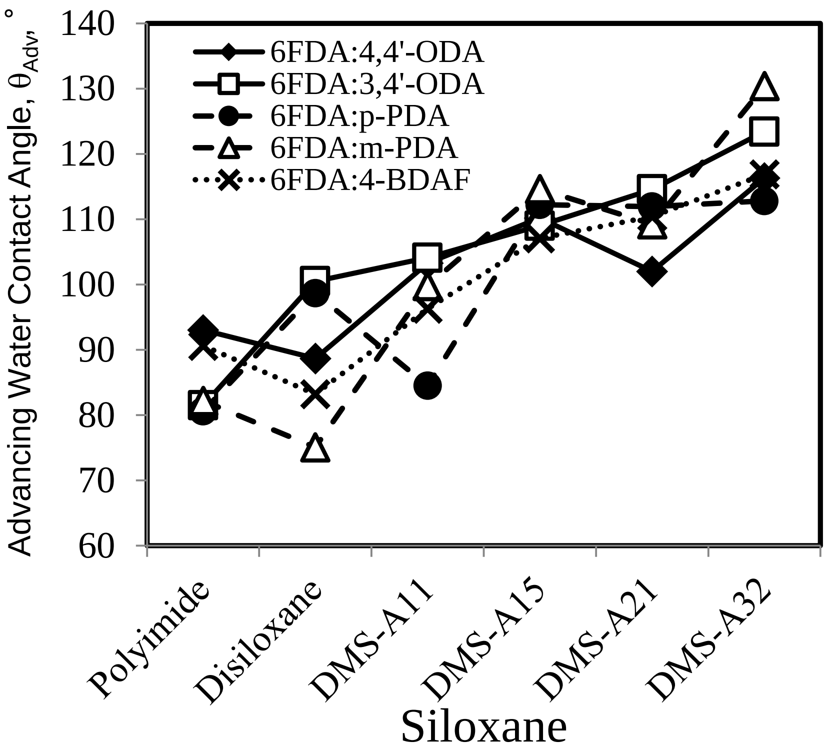
Surface Migration

- Entropy vs enthalpy

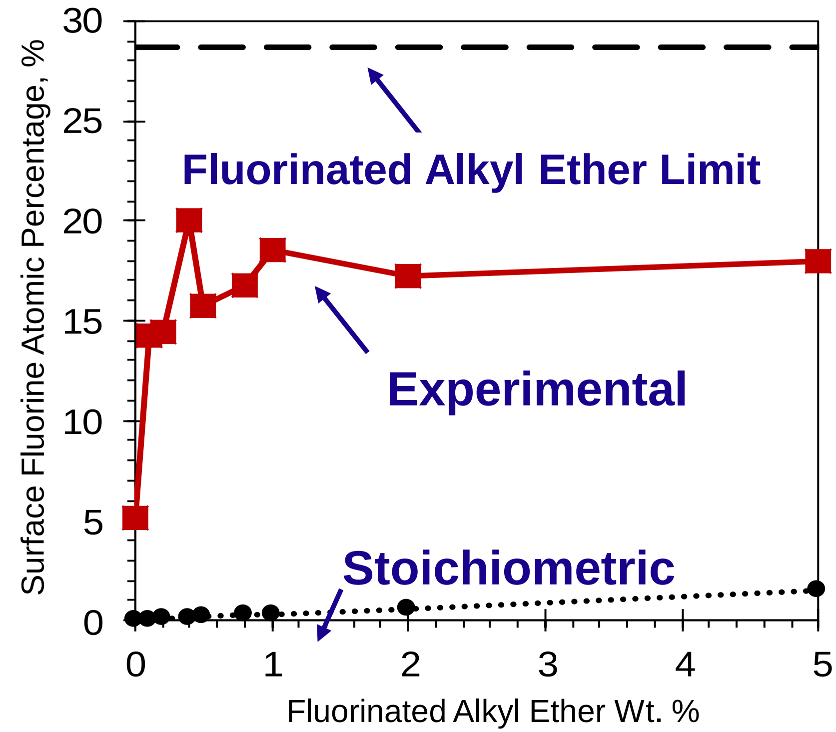


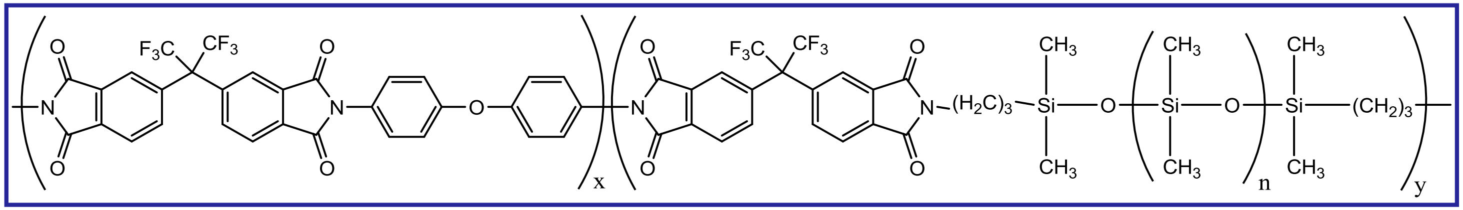
Copolyimides with SMAs

Si-containing Polyimides



F-containing Polyimides

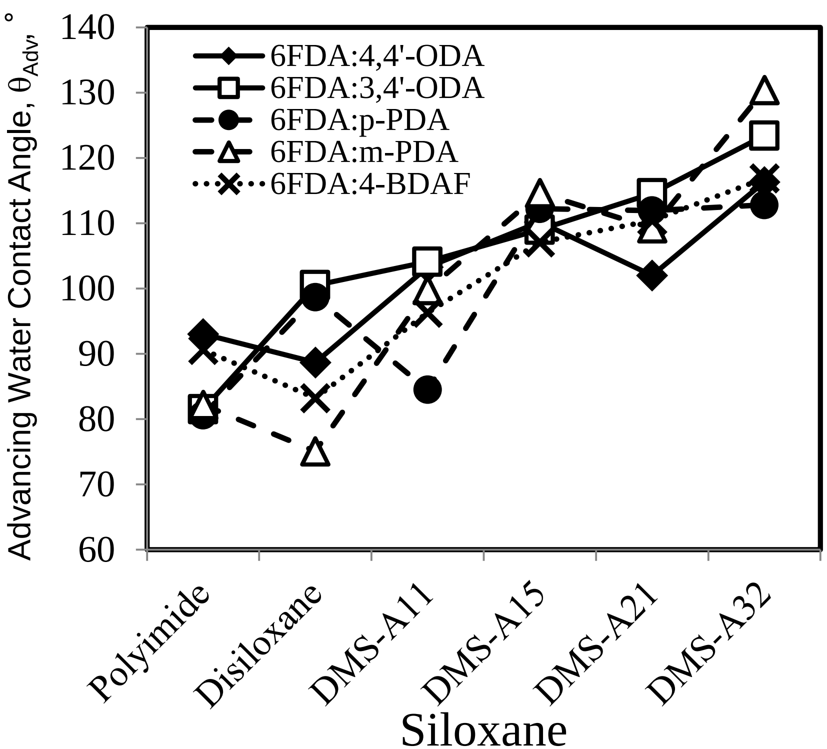




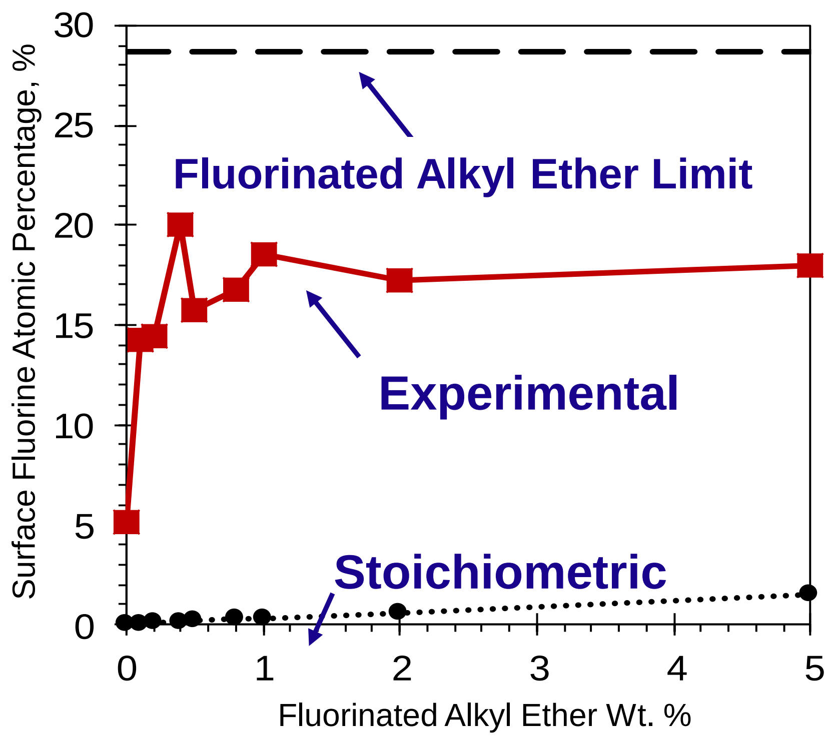
Wohl, et. al. *High Perform. Polym.* **2012**, *24(1)*, 40-49. Wohl, et. al. *J. App. Polym. Sci. B.*, **2015**, *132(9)*, 41538.

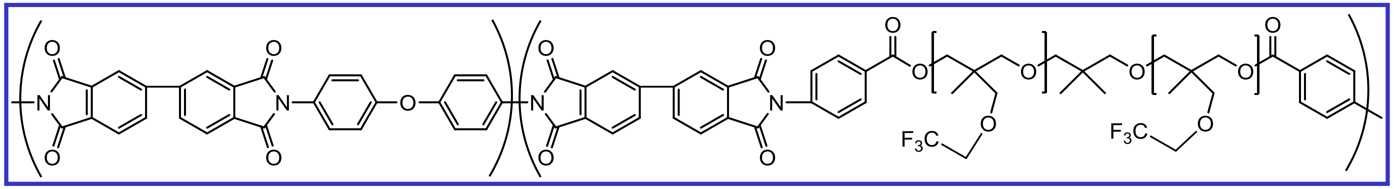
Copolyimides with SMAs

Si-containing Polyimides



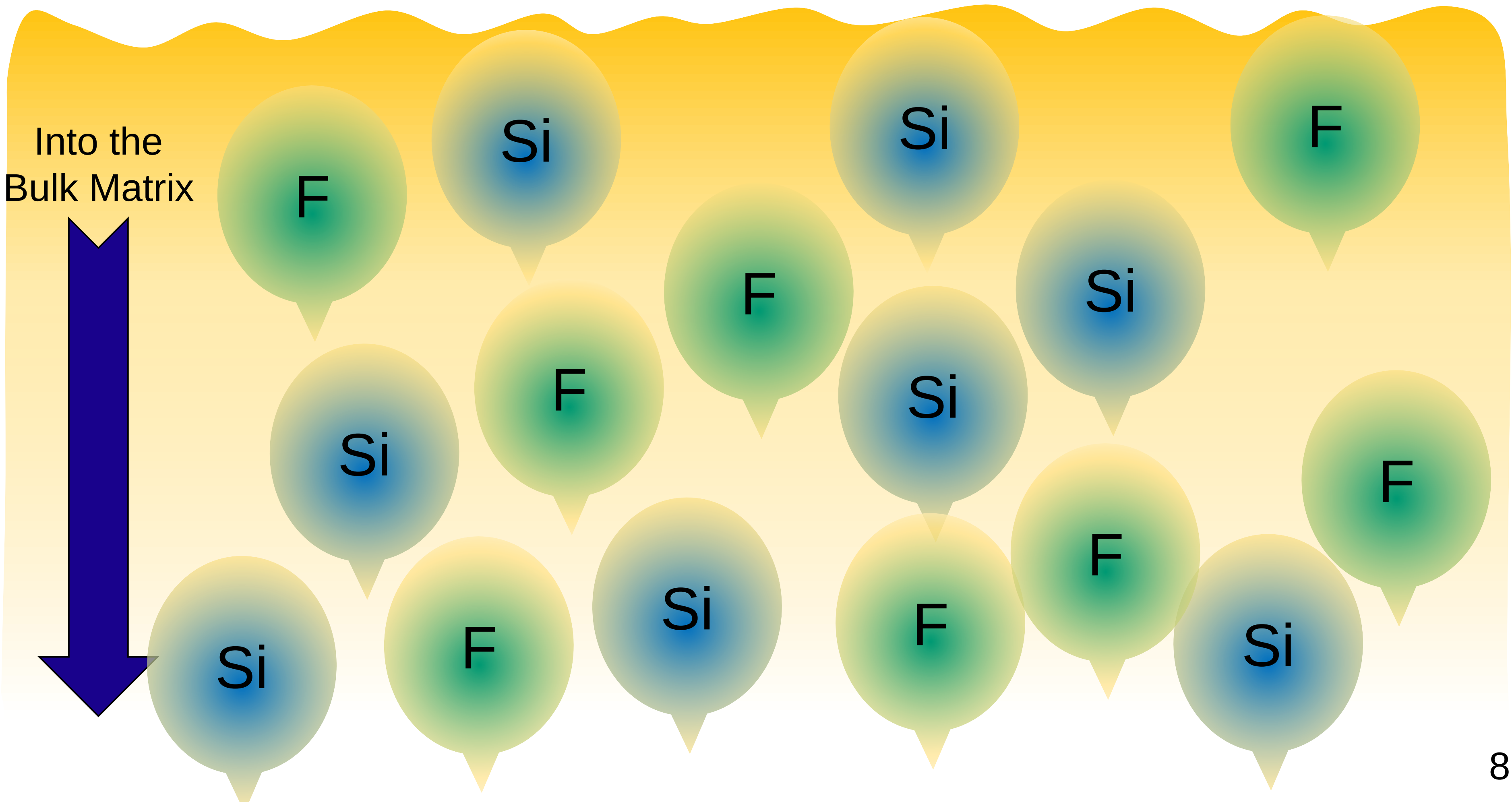
F-containing Polyimides



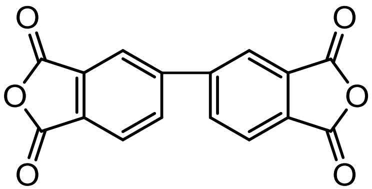


Wohl, et. al. *High Perform. Polym.* **2012**, *24(1)*, 40-49. Wohl, et. al. *J. App. Polym. Sci. B.*, **2015**, *132(9)*, 41538.

What Happens when Two SMAs Compete?

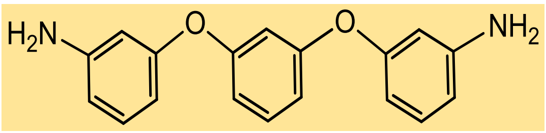


Synthesis of CoPoly(Imide Oxetane Siloxane)-PIOS



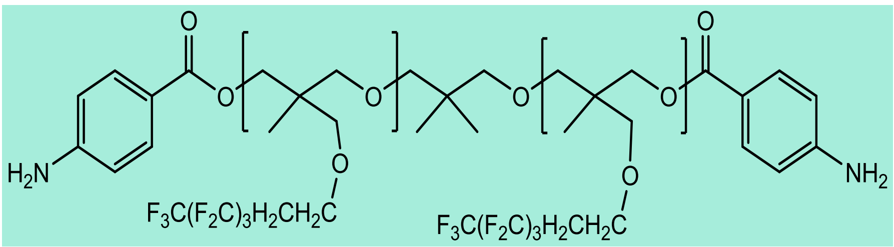
s-BPDA

+



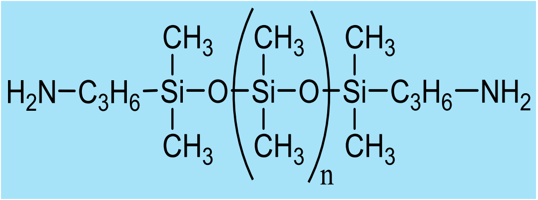
1,3,3-APB

+



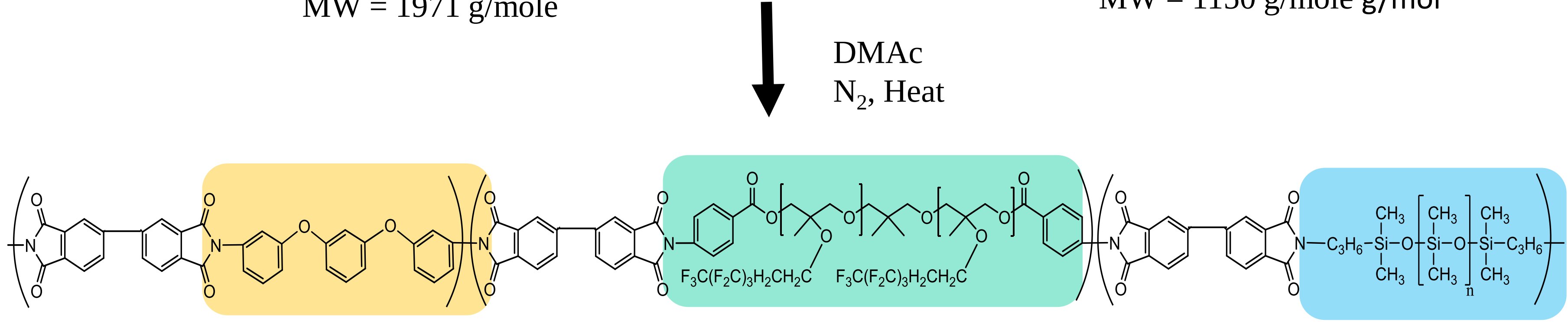
PolyFox7002 (**AEFO**)
MW = 1971 g/mole

+



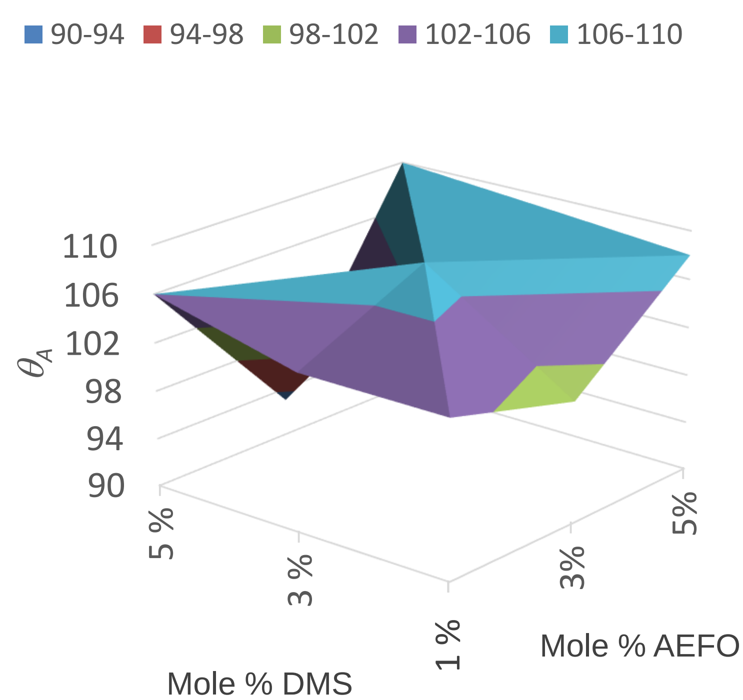
DMS-A11
MW = 1150 g/mole g/mol

DMAc
N_2, Heat



SMAs Influence on Contact Angle

Designation	Stoichiometric Composition, Mole % of Monomer		Advancing Water Contact Angle, θ_A	
			Air Side	Plate Side
BPDA Control	BPDA and APB		89	90
BPDA-1	5% AEFO,	5% DMS	114	108
BPDA-2	1% AEFO,	1% DMS	103	92
BPDA-3	3% AEFO,	3% DMS	108	98
BPDA-4	5% AEFO,	1% DMS	106	94
BPDA-5	1% AEFO,	5% DMS	108	102
BPDA-6	5% AEFO,	3% DMS	93	120
BPDA-7	3% AEFO,	5% DMS	109	112
BPDA-8	0.5% AEFO,	0.5% DMS	105	117
BPDA-9	3% AEFO,	1% DMS	103	109
BPDA-10	1% AEFO,	3% DMS	100	94



Electron Dispersive Spectroscopy (EDS)

Increased disparity in F concentration

Increased Si plate surface concentration

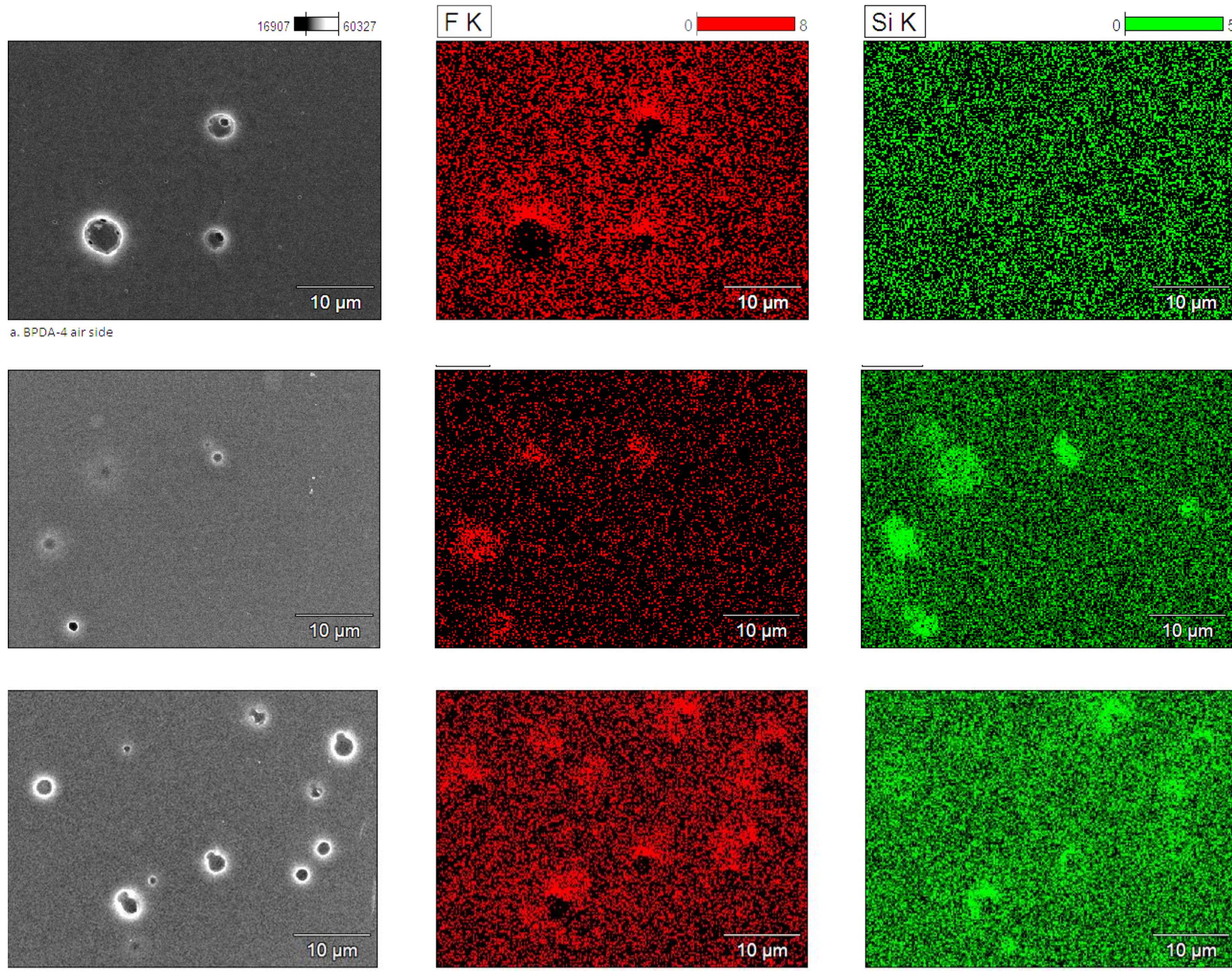
Sample	% AEFO	% Si		C (wt%)	O (wt%)	F (wt%)	Si (wt%)
BPDA-3	3	3	Air	31.8	41.5	13.3	5.0
			Plate	31.0	38.3	16.1	6.7
BPDA-4	5	1	Air	29.2	42.0	18.8	1.6
			Plate	26.2	30.6	35.1	2.2
BDPA-5	1	5	Air	31.9	43.0	9.1	7.3
			Plate	32.2	44.2	8.6	6.4
BPDA-6	5	3	Air	30.7	40.0	15.6	5.2
			Plate	25.6	27.5	36.0	5.1
BPDA-7	3	5	Air	29.6	37.6	17.4	7.5
			Plate	27.4	35.9	18.8	10.7

N content varied between 6 and 9%

EDS Mapping: Air Side

- **BPDA-4**
  - 5% AEFO, 1% DMS
- **BPDA-5**
  - 1% AEFO, 5% DMS
- **BPDA-7**
  - 3% AEFO, 5% DMS

All % values are mole % monomer

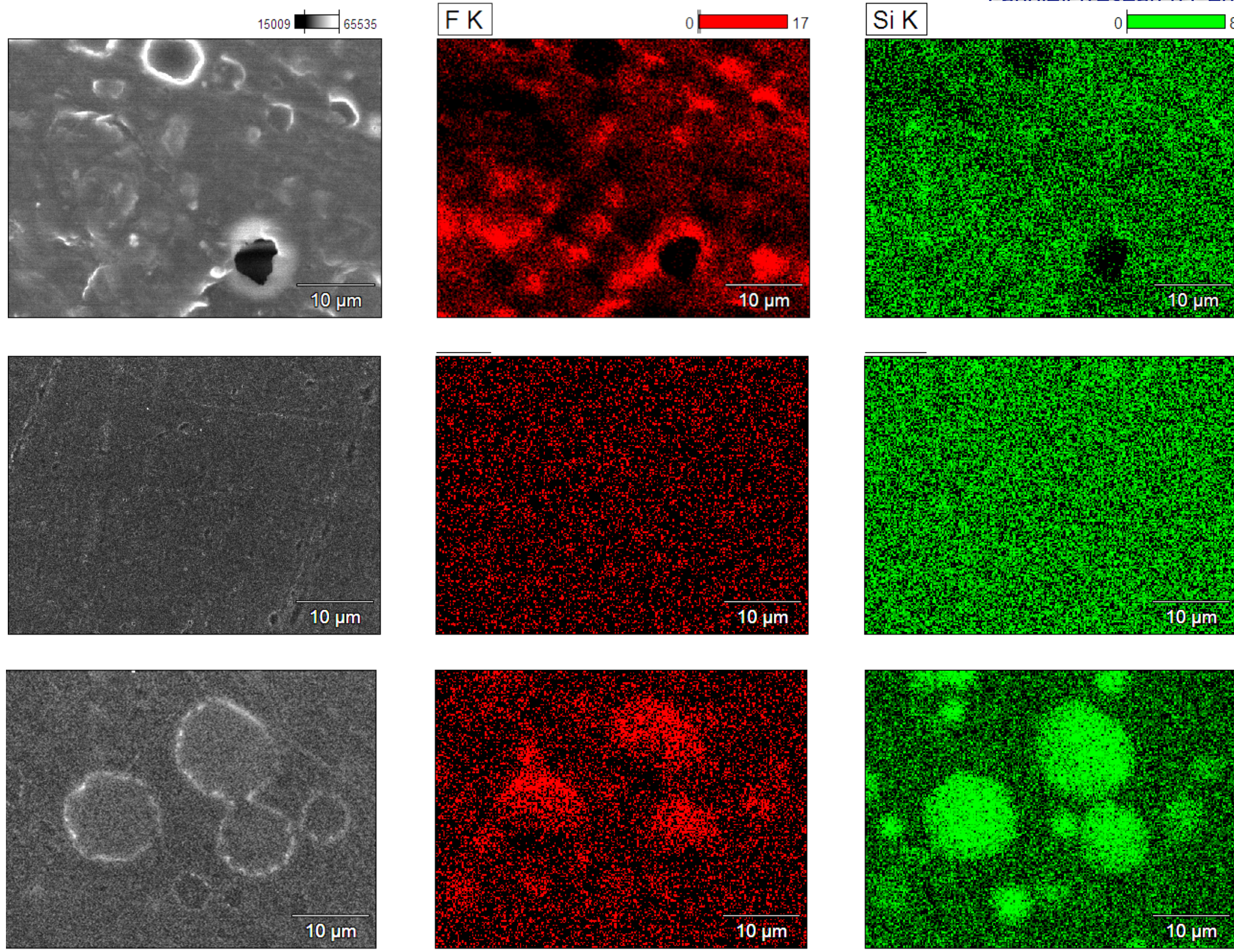


Nominal DMS-Mediated Domain Formation

EDS Mapping: Plate Side

- **BPDA-4**
  - 5% AEFO, 1% DMS
- **BPDA-5**
  - 1% AEFO, 5% DMS
- **BPDA-7**
  - 3% AEFO, 5% DMS

All % values are mole % monomer



Obvious AEFO-Mediated Domain Formation

SMAs Influence on Contact Angle

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Designation	Stoichiometric Composition, Mole % Monomer	Advancing Water Contact Angle, θ_A	
		Air Side	Plate Side
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BPDA-1	5% AEFO, 5% DMS	114	108
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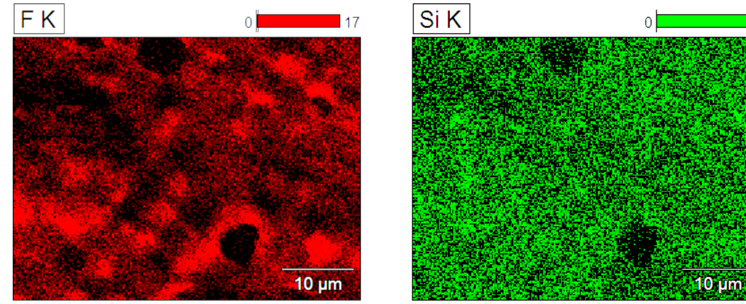
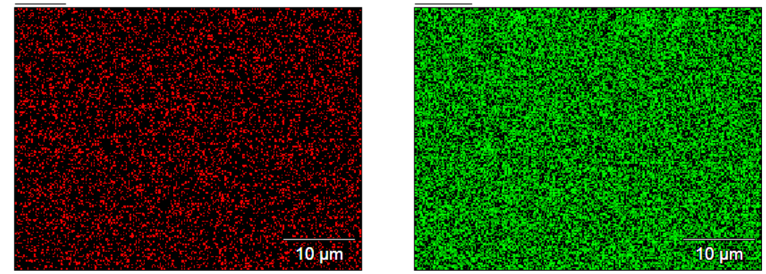
BPDA-8	0.5% AEFO, 0.5% DMS	105	117
BPDA-9	3% AEFO, 1% DMS	103	109
BPDA-10	1% AEFO, 3% DMS	100	94

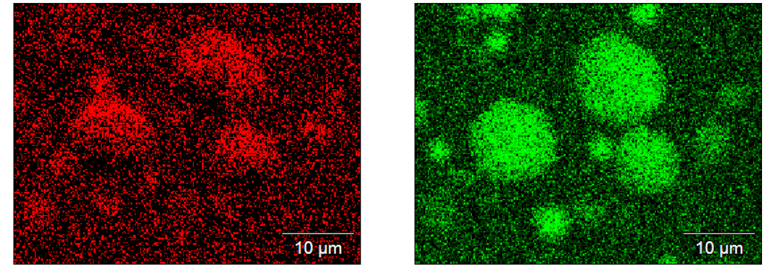
Plate Side



BPDA-4

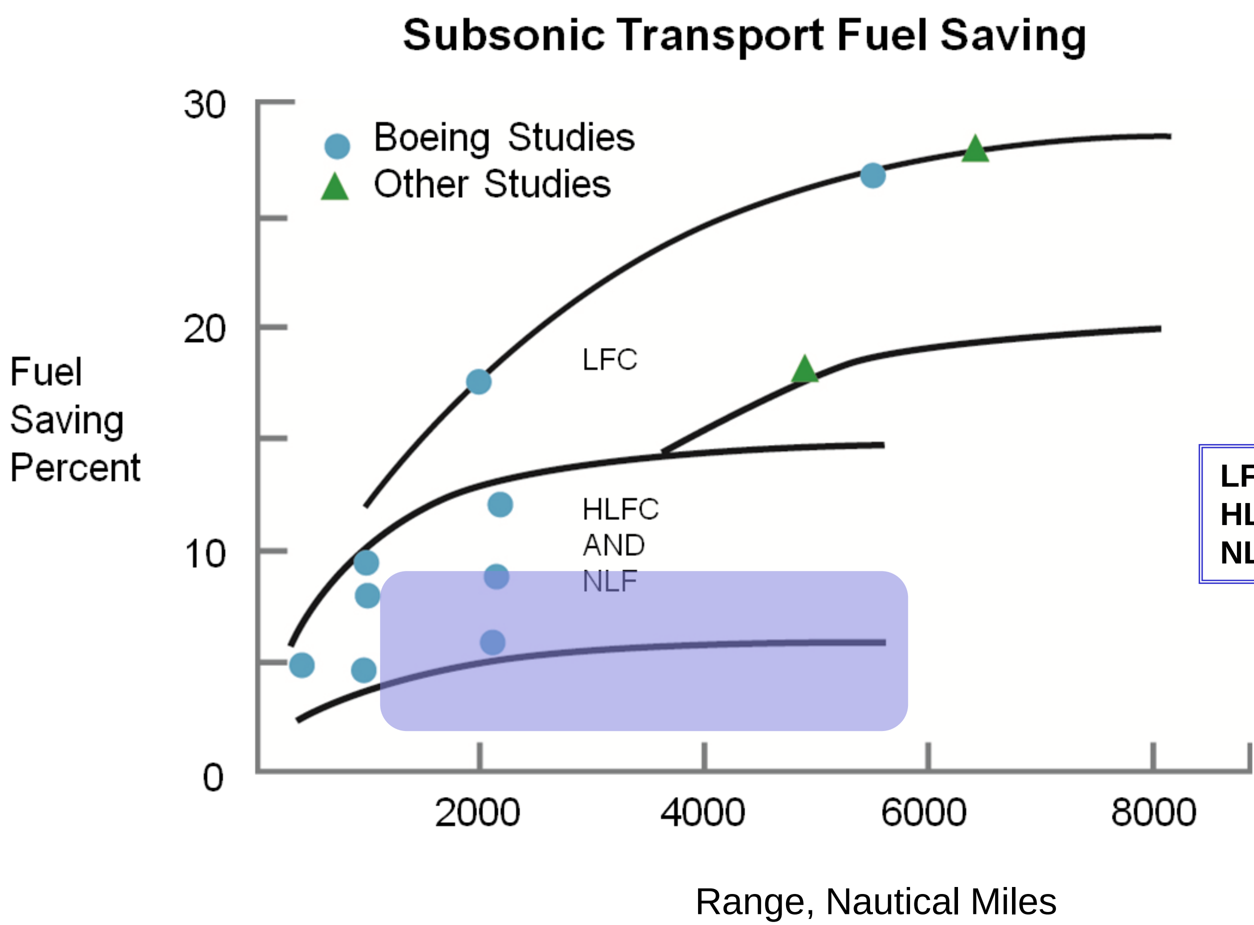


BPDA-5



BPDA-7

Natural Laminar Flow Saves Fuel



LFC: Laminar Flow Control
HLFC: Hybrid Laminar Flow Control
NLF: Natural Laminar Flow

Kirchner, M.E. NASA CP-2487, 1987, Part 1, pp. 24-44.

What we know about Insect Adhesion Mitigation …

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- **Existing commercial materials are not effective**

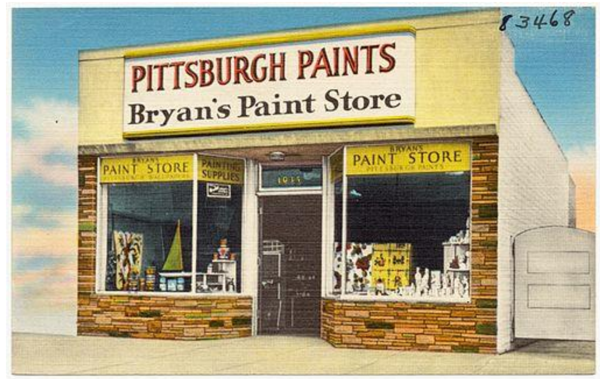

Image from Wikimedia Commons
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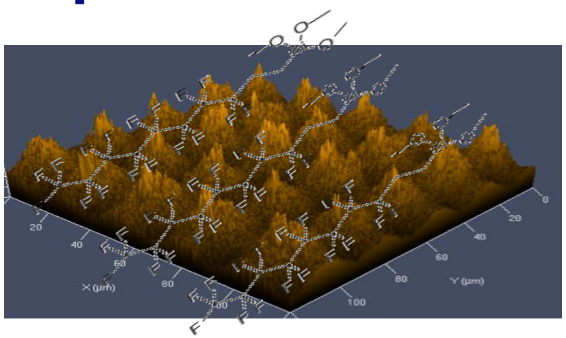
- **Both surface chemistry and surface topography are important**



- **Results are dependent on evaluation method**

Wohl, et. al. *Prog. Org. Coat.* **2013**, *76*, 42-50. Kok, et. al. *Prog. Aerospace Sci*. **2015**, *75*, 1-14.

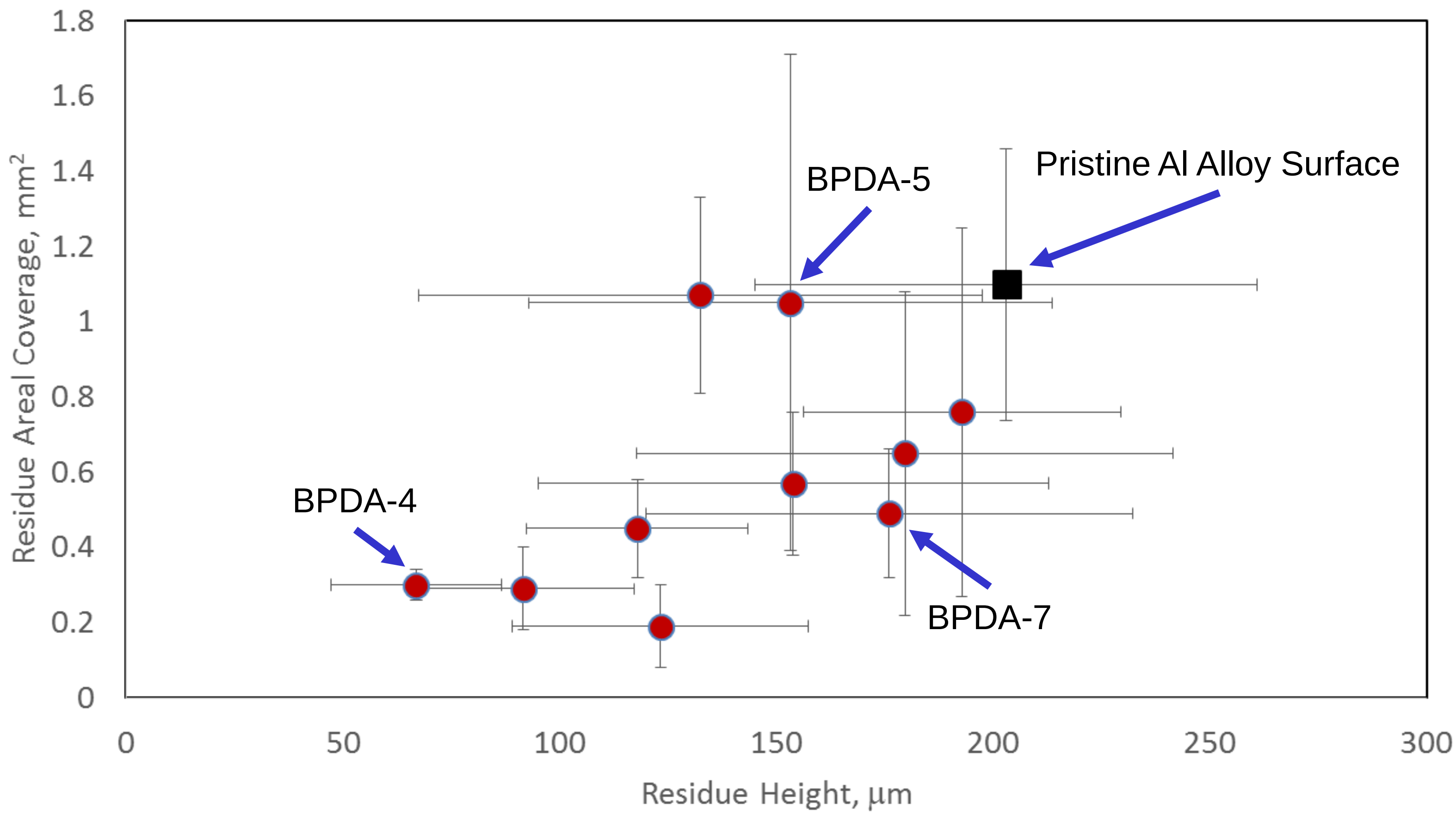
Operational Environment Simulation

Flightless fruit fly (*drosophila melanogaster*)

Bench-top Wind Tunnel

High Speed Photography

Fruit Fly Residue Characterization



Data collected using a non-contact optical profilometer (Microprof 100FRT of America)

SMA Codependence, Constant AEFO

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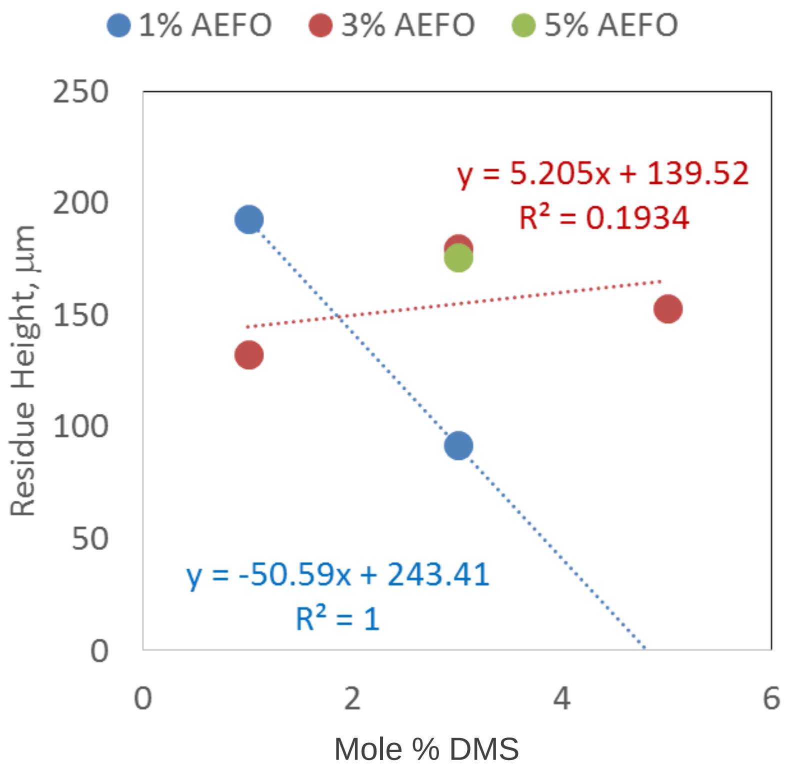
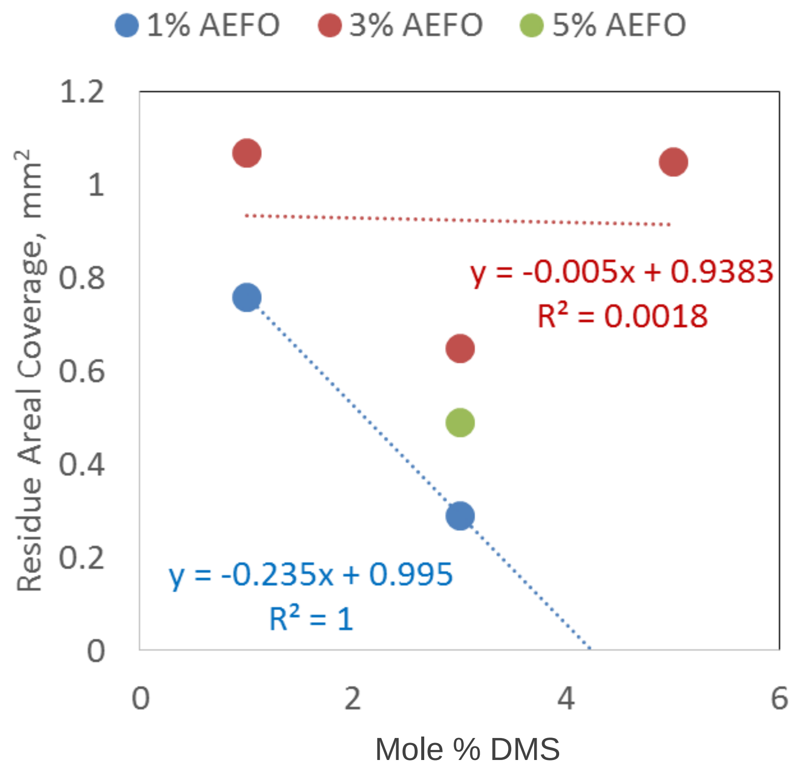
Residue Height



Residue Areal Coverage



All % values are mole % monomer

Based on available data, no clear dependence of remaining insect residue on Si content variation

SMA Codependence, Constant Si

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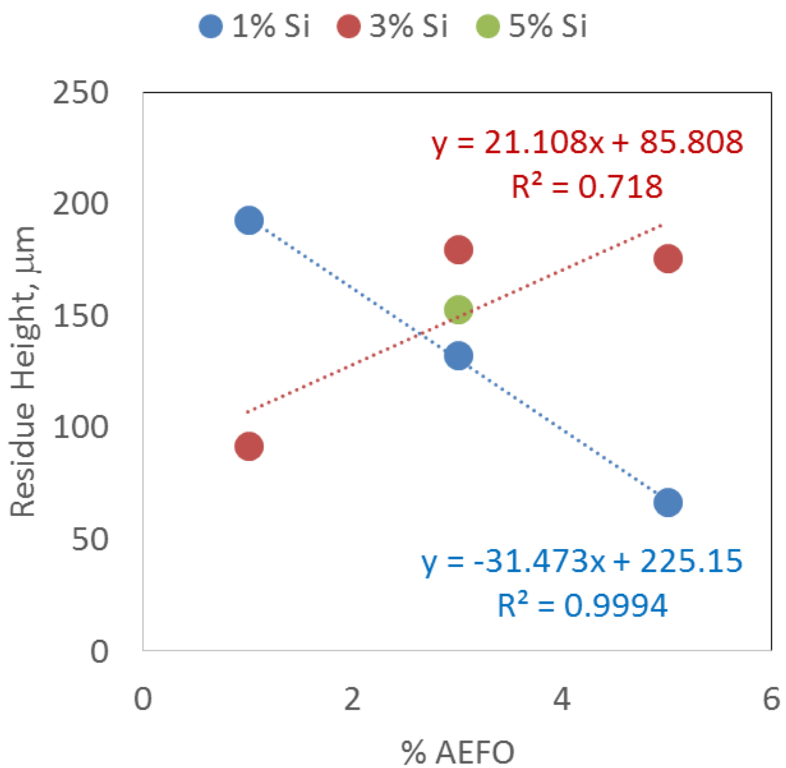
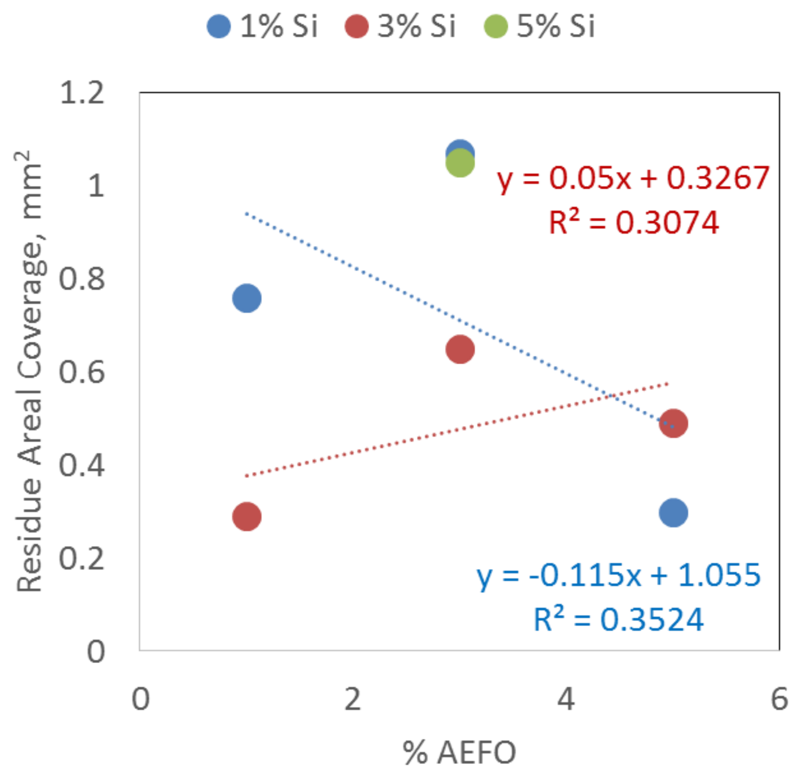
Residue Height



Residue Areal Coverage



All % values are mole % monomer

- At low Si content, increased AEFO was **beneficial**
- At increased Si content, increased AEFO was **detrimental**

Summary & Future Work

- **Summary**
  - Inclusion of 2 SMAs revealed:
    - Preferential migration of AEFO to the glass side
    - AEFO facilitating DMS surface migration to the glass side
  - Differences in θ_A attributed to SMA concentration and copolymer segregation at the surface
  - Both SMAs interact to change insect residue adhesion and the net effect is still difficult to ascertain

- **Future Work**
  - Explore more AEFO/DMS combinations including lower weight % values
  - Collect more insect impact data
  - Explore surface mechanical properties as they relate to SMA content

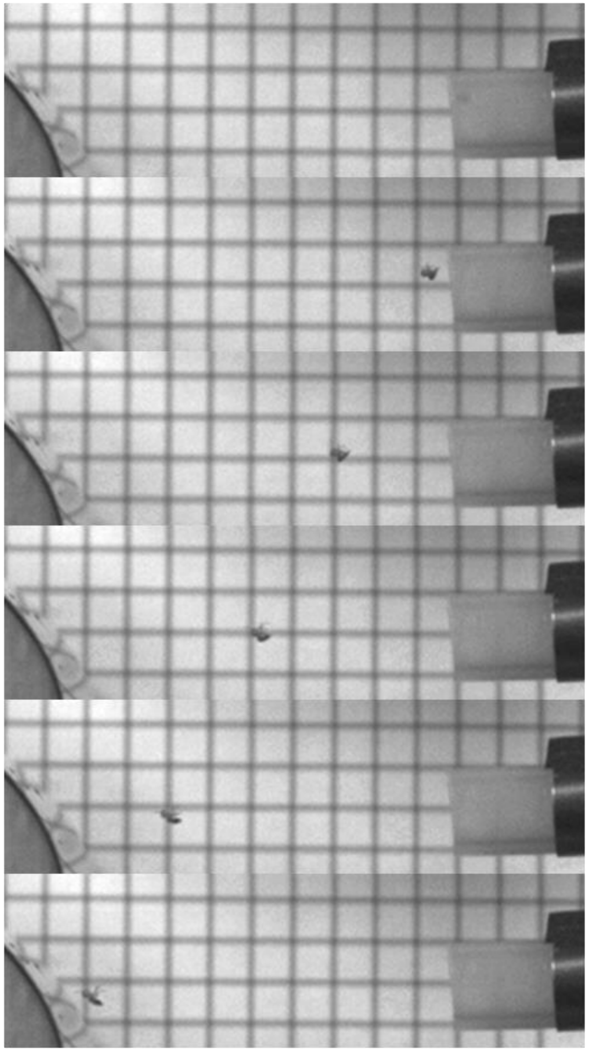
Acknowledgements

The authors would like to thank:

- Other members of the ERA team: Emilie Siochi, Joseph Smith, Ronald Penner
- Paul Bagby for high speed photography
- The National Institute of Aerospace
- The Langley Aerospace Research Summer Scholars Program
- The ACS Division of Polymer Chemistry

Supplementary Slides

Fruit Fly Velocity Determination



t = -60 μs

t = 0 μs

t = 160 μs

t = 300 μs

t = 460 μs

t = 600 μs